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| 氏 名        | KWASI OSAFO AMPADU  |
| 生 年 月 日    |   |
| 本 籍        | ガーナ   |
| 学 位 の 種 類  | 博士(工学)  |
| 学 位 記 番 号  | 博甲第498号   |
| 学位授与の日付    | 平成14年3月22日  |
| 学位授与の要件    | 課程博士(学位規則第4条第1項)  |
| 学位授与の題目    | A Study on the Characterization of Ecocement Produced from Incinerated Ashes and the Corrosive Behavior of Steel Bars in Ecocement Mortars (都市ゴミ焼却灰より製造したセメントの性質とモルタル中の鉄筋の腐食性状に関する研究) |
| 論文審査委員(主査) | 鳥居 和之(工学部・教授)   |
| 論文審査委員(副査) | 川村 満紀(工学部・教授) 梶川 康男(自然科学研究科・教授)<br>五十嵐心一(工学部・助教授) 佐伯 竜彦(新潟大学工学部・助教授)  |

## 学 位 論 文 要 旨

### ABSTRACT

Ecocement is new-type hydraulic cement produced through recycling of wastes. This new cement is designed to use incinerator ashes up to 50 % of raw materials. The main objective of the research work undertaken in this thesis is to ascertain the strength and durability of ecocement as a building material. The first part of the study was on the characterization of ecocement and its hydration products. This was followed by another study on the corrosive behavior of steel bars embedded in ecocement mortars placed under various environmental conditions and finally, the beneficial effect of blast-furnace slag and fly ash on chloride-induced corrosion of steel bars embedded in ecocement mortars was also studied. In addition, a parallel study on the chloride diffusivity through concretes/mortars made with OPC incorporating fly ash and blast-furnace slag was also studied and the results compared with that of ecocement.

### 1. Introduction

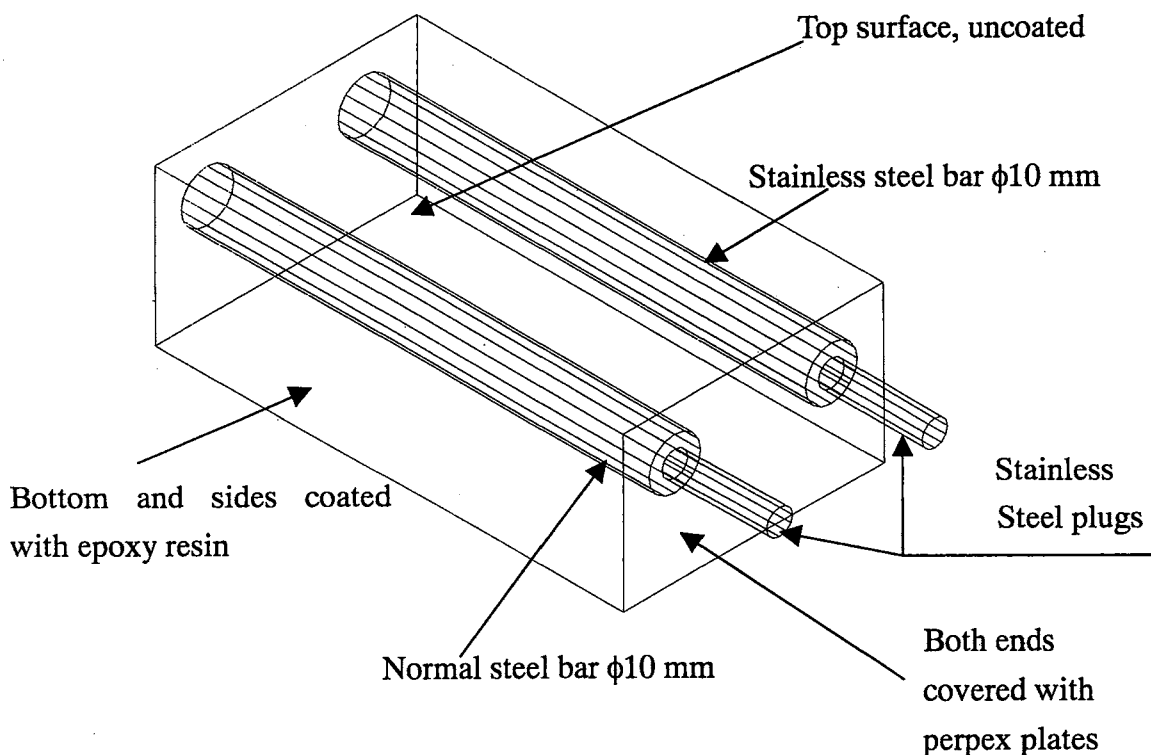
Ecocement is a new type hydraulic cement, and like all new products, especially building materials that are intended to be used to build structures with service life of 50 years or more, experimental testing is required to ascertain its strength and more importantly, its durability. Research work undertaken for this PhD thesis is in this regard.

### 2. Experimental Modules

The study on ecocement was conducted in 3 modules as follows:

- (1) Characterization of ecocement and its hydration process [1].
- (2) Corrosive behavior of steel bars embedded in ecocement mortars under various environmental Conditions [2] [3].
- (3) Beneficial effect of blast-furnace slag and fly ash on chloride induced corrosion of steel bars embedded in ecocement in comparison to OPC Mortars.

In addition, another study was performed on the evaluation of chloride permeability of concretes incorporating fly ash and blast furnace slag. Ordinary Portland cement (OPC) was used for this part of the study.



**Fig. 1** Schematic diagram of test specimen

### 3. Experimental Methods used in this study

Ecocement pastes and mortars were prepared at various water to binder ratios. The specimens for microstructure characterization and also for the determination of mechanical properties were cured in saturated calcium hydroxide solution. **Fig. 1** shows a diagram of the specimens used to study the corrosive behavior of steel bars embedded in ecocement mortars.

In the characterization of ecocement pastes/mortars, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), differential scanning calorimetry (DSC), electrical resistivity, AC impedance spectroscopy and compressive strength were the test methods employed. In the study of the corrosive behavior of steel bars embedded in ecocement mortars, electrochemical measurements such as the half-cell potential, linear polarization resistance and AC impedance were used.

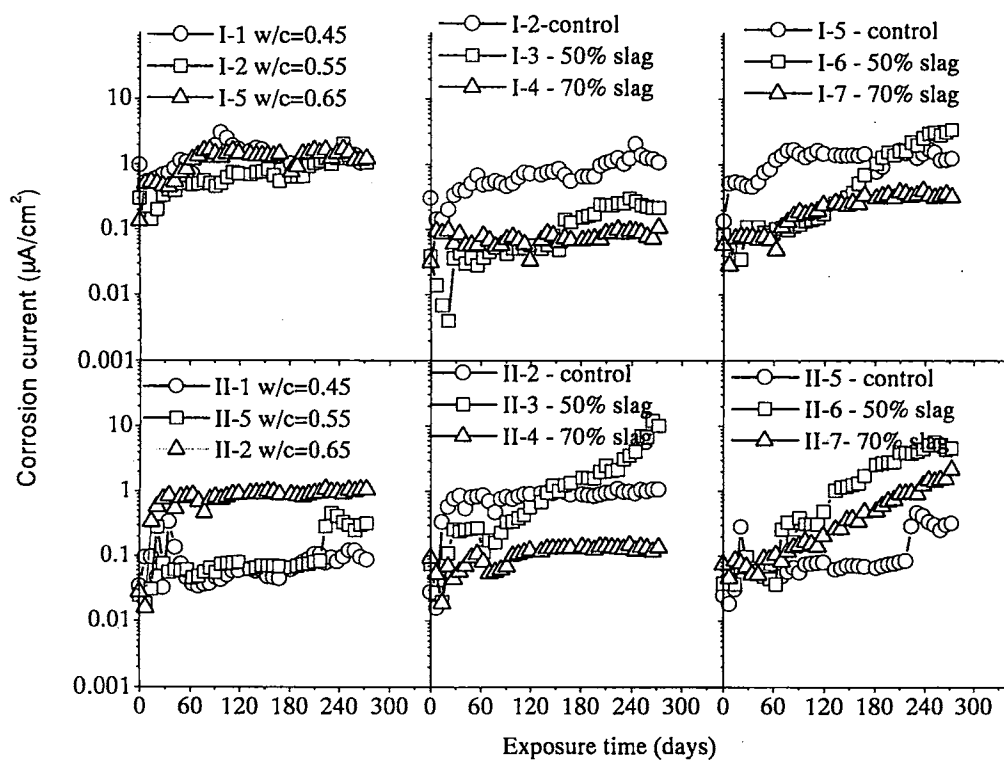
Physical measurements such as mass loss and corroded areas were also used to validate the results of the electrochemical measurements.

In the study of the beneficial effects of mineral admixtures like fly ash and slag on ecocement, SEM, DSC and XRD were used to characterize the mortars/pastes. The diffusivity of the mortars was determined by measuring the chloride concentration profiles in the ecocement-slag/fly ash mortar specimens.

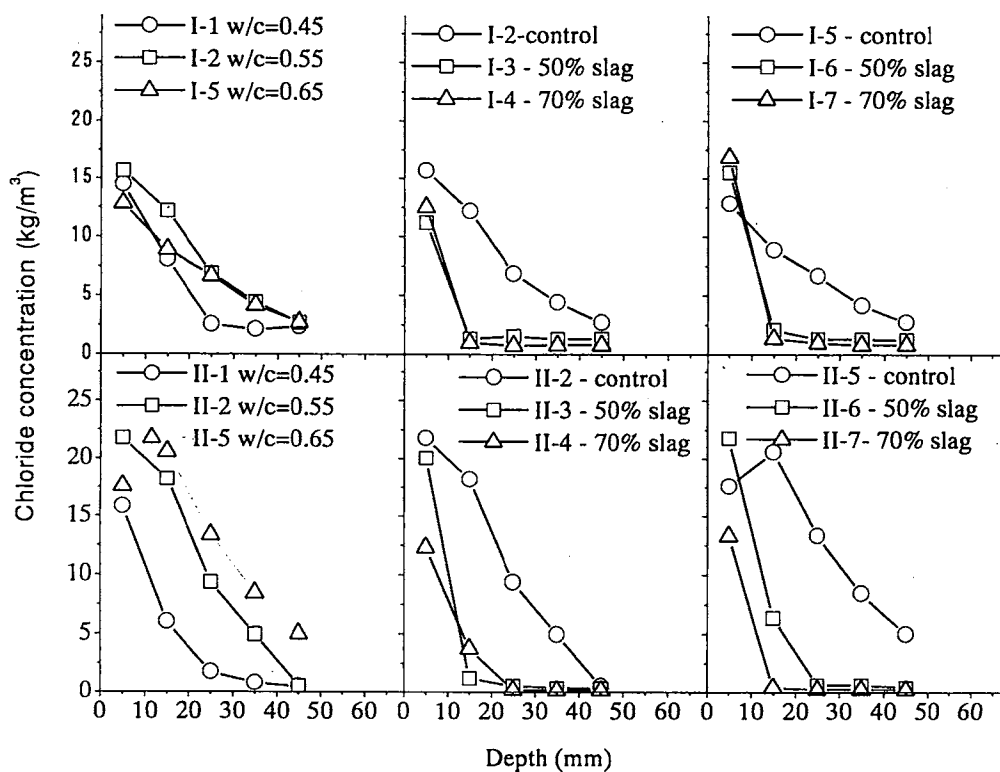
### 4. Typical Results of the Study

#### 4.1 Corrosion Current

**Fig. 2** shows the variations of corrosion current with exposure time for the steel bars embedded in the ecocement Types I and II mortars placed in a severe saline environment. It is seen that in the case of the ecocement Type I specimens, the addition of slag at w/b of 0.55 results in a reduction in the corrosion current, however at



**Fig. 2** Corrosion current versus exposure time for steel bars embedded in ecocement mortars placed under saline environment



**Fig. 3** Chloride concentration versus depth from the surface of ecocement Types I and II mortars

a w/b of 0.65, as much as 70% slag is required for this benefit to be realized. On the other hand, in the case of ecocement Type II specimens, at w/b of 0.55, as much as 70% slag replacement resulted in a reduction in the corrosion current, however, at w/b of 0.65, the slag seems to have an adverse effect.

#### **4.2 Chloride Concentration Profiles**

**Fig. 3** shows the chloride concentration profiles of the ecocement-slag mortars placed in a severe saline environment. It is seen that in both types of ecocement, the addition of the slag results in a reduction in the chloride profiles, indicating lowering of porosity. The graphs also show that, the chloride profiles increases with w/b.

### **5. Summary of Conclusions**

#### **5.1 Hydration characteristics and microstructure**

In the hydration of both ecocement Type I and II, the amount of calcium hydroxide formed in the Type I is less than that of the Type II, which in turn is less than that of OPC. Also ettringite is formed in the hydration of ecocement as against mono-sulfo aluminate hydrate. Small amount of Friedel's salt is formed in the Type I, thus, binding some of the inherent chloride.

#### **5.2 Corrosive behavior of steel bars embedded in mortars under various environmental conditions**

Under wetting and drying conditions, the corrosivity of steel bars embedded in Type I ecocement mortars of high w/c are higher than that embedded in Type II mortars due to the high chloride content of the former.

Under severe saline environment, steel bars embedded in the Type I ecocement mortars corrode to a greater extent than the Type II, which is also greater than that of OPC.

When both the mortars of both ecocements Type I and II were exposed to accelerated carbonation condition, it was observed that the mortars of Type I were more susceptible to neutralization than that of Type II.

#### **5.3 Protective measures against corrosion**

##### **5.3.1 Effect of blast-furnace slag on ecocement mortars**

Blending ecocement with ground granulated blast-furnace slag improves the microstructure of the resulting mortars in a similar manner to OPC. The higher the slag replacement ratio, the better the improvement. However, the extent of microstructure improvement in ecocement-slag paste is less than that of corresponding OPC pastes.

In the mortars of Type I ecocement, large amount of slag replacement and low w/b is required for any improvement with respect to corrosion of embedded steel bars to be manifested. In Type II ecocement, the addition of slag rather causes a negative effect at moderate to high w/b in a severe saline (5%) environment

##### **5.3.2 Effect of low quality fly ash on ecocement mortars**

The addition of low quality fly ashes to both OPC and ecocement Type I results in mortars with lower chloride ingress, however, there was an adverse effect on the corrosive behaviors of the embedded steel bars, probably due to the shallow cover depth (10 mm) of the steel bars. Also, at 20% replacement by the low quality fly ashes, there was only a slight reduction in compressive strength, however at 40% replacement there was a significant reduction in strength in the mortars of both cements.

On the monitoring methods used in this study it was observed that AC

impedance spectroscopy is a useful tool in the monitoring of micro-structural development of mortars as well as the corrosive behavior of steel bars embedded in the mortars.

## References

- [1] Ampadu K.O, Torii, Characterization of Ecocement Pastes and Mortars Produced from Incinerated Ashes, Int. J. of Cement and Concrete Research, Vol. 31, No.3, pp. 431-436 (2001)
- [2] Ampadu K.O, Torii, K. Kubota, T. A Preliminary Study on Chloride Induced Steel Corrosion of Ecocement Mortar Produced from Incinerator Ash Under Wetting and Drying Conditions, Concrete under severe Conditions, Proceedings of International Conference (CONSEC'01) pp. 293 – 300 (2001).
- [3] Ampadu, K.O., Torii, K., Chloride Induced Corrosion of Steel Bars Embedded in Ecocement-Blastfurnace Slag Mortars, Proceedings of the 7<sup>th</sup> CANMET/ACI International Conference on Fly Ash, Slag, Silica Fume and Natural Pozzolans in Concrete, held in Madras, (2001).

## 学位論文審査結果の要旨

本学位論文に関して、平成 14 年 1 月 22 日に第 1 回の審査委員会を開催し、論文の内容を検討した。また、2 月 1 日の口頭発表の後に、第 2 回の審査委員会を開催し、協議した結果、以下のように判定した。

エコセメントは都市ゴミ焼却灰や下水汚泥を原料として製造する、資源循環型のセメントで、平成 13 年に国内最初のエコセメントの製造プラントが千葉県の市原市に完成している。エコセメントの化学成分及び鉱物組成は通常のポルトランドセメントとは大きく相違する。このため、本論文では、まずエコセメントの鉱物組成と水和反応生成物の特徴について詳細に検討し、エコセメントを用いたモルタルの強度発現性状及び細孔径分布を明らかにしている。一方、エコセメントには、塩化物イオンが含まれており、コンクリート構造物に使用した際には鉄筋腐食への影響が重要となる。このため、本論文では、乾湿繰り返し及び塩水噴霧の 2 種類の環境下にて、エコセメントを使用したモルタル中の鉄筋の腐食性状を長期間にわたり調べ、エコセメントの鉱物組成及び塩化物イオンの含有量がモルタル中の鉄筋の腐食性状に及ぼす影響を明らかにしている。また、産業副産物である高炉スラグ微粉末及びフライアッシュをエコセメントに混入することによる、モルタルの強度発現及び鉄筋腐食の改善効果についても貴重な研究成果を得ている。研究成果は、今後汎用セメントとして普及することが予想される、エコセメントの実用化及びその品質規準の確立に大きく貢献するものである。以上を総合して、審査委員会は、本論文を博士（工学）の学位を与えるのに十分な内容を有していると判断した。